

Spin singlet pairing in the superconducting state of $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$: evidence from a ^{59}Co Knight shift in a single crystal

Guo-qing Zheng¹, Kazuaki Matano¹, D.P. Chen², and C.T. Lin²

¹ *Department of Physics, Okayama University, Okayama 700-8530, Japan and*

² *Max Planck Institute, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

We report a ^{59}Co Knight shift measurement in a single crystal of the cobalt oxide superconductor $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ ($T_c = 4.25$ K). We find that the shift due to the spin susceptibility, K^s , is substantially large and anisotropic, with the spin shift along the a -axis K_a^s being two times that along the c -axis K_c^s . The shift decreases with decreasing temperature (T) down to $T \sim 100$ K, then becomes a constant until superconductivity sets in. Both K_a^s and K_c^s decrease below T_c . Our results indicate unambiguously that the electron pairing in the superconducting state is in the spin singlet form.

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The recently discovered superconductivity in cobalt oxide $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ has attracted considerable attention¹. The new material consists of two-dimensional CoO_2 layers that bear similarity to high temperature (high- T_c) copper oxide superconductors. A simple but wide-spread view of the electronic state is that increasing the sodium content x adds x electrons to the spin 1/2 network in the CoO_2 layer^{2,3}, which is similar to the case of doping the spin 1/2 network in the CuO_2 layer of the high- T_c cuprates. However, there is a large difference between these two classes of transitional-metal oxides. Namely, Co forms a triangular lattice in the cobaltate, instead of square lattice in the cuprates. Because of this crystal structure, exotic superconducting states are expected in the cobaltate. So far, chiral d -wave, p -wave, f -wave and i -wave states^{2,3,4,5,6,7,8,9}, as well as odd-frequency s -wave state¹⁰ have been proposed theoretically. The d - and i -wave states are spin singlet states, while the remainder are spin triplet states.

Indeed, the nuclear spin-lattice relaxation rate ($1/T_1$) measurements by us indicate that the superconducting state is unconventional; $1/T_1$ is proportional to T^3 below the transition temperature T_c , suggesting line nodes in the gap function^{11,12}. However, the symmetry of the spin pairing has been unclear. Previous measurements of the angle-averaged Knight shift in powder samples have resulted in controversial conclusions^{13,14}. Kato *et al* reported no change of the shift below T_c ¹³, while Kobayashi *et al* found a decrease of the shift in a powder sample¹⁴. The former suggested triplet pairing, while the latter concluded to s -wave pairing. The difficulty in growing the samples, which often accompany a secondary phase that gives rise to a spurious NMR peak overlapping the main peak in question, complicates the data analysis in powder samples. Therefore, measurements of the spin susceptibility via the Knight shift in single crystals are required.

In particular, the Knight shift in the c -axis direction is essential to distinguish various pairing states proposed theoretically^{2,3,4,5,6,7,8,9,10}. This is because even for triplet pairing, the spin susceptibility in the a -axis direction can be reduced below T_c but that along the c -axis direction should remain unchanged across T_c ¹⁵.

Kobayashi *et al* have attempted to align small single crystal platelets¹⁶, but their samples contain multiple phases with almost equal amount of non-superconducting composition that contaminated the NMR signal observed. So far, no work has been reported to determine the absolute value of the c -axis shift due to the spin susceptibility which is important in discussing the superconducting state properties.

In this paper, we report the first complete data set of the ^{59}Co Knight shift in a high quality *single crystal* with $T_c = 4.25$ K. We find that the spin contribution to the Knight shift is significantly large and anisotropic. The spin Knight shift along both the a -axis and c -axis decrease below T_c . Our results indicate unambiguously that the spins that form the Cooper pairs in the superconducting state are anti-parallel.

Single crystal of $\text{Na}_{0.42}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ used in this study was grown by the traveling solvent floating zone (TSFZ) method, as described in a previous publication¹⁷. AC susceptibility measurement using the in-situ NMR coil indicates that the T_c at zero magnetic field is 4.25 K (data not shown). NMR experiments were performed using a home-built phase-coherent spectrometer. The NMR spectra were taken by changing the external magnetic field (H) at a fixed RF frequency and recording the echo intensity step by step.

Figure 1 shows a typical example of the NMR spectra for $H \parallel c$ -axis and $H \parallel a$ -axis. As can be seen in Fig. 1(a), a sharp central transition line accompanied by six satellites due to the nuclear quadrupole interaction, are observed. There is essentially no signal intensity between the sharp peaks, which indicates good quality of the single crystal.

Figure 2 shows the temperature dependence of the Knight shift K_a with the field applied along the a -axis, and K_c with the field applied along the c -axis. K_c was determined from the central peak as well as from the midpoint between the two first satellites; results obtained by the two procedures agree well¹⁸. K_a was determined from the central transition, by taking into account the shift due to quadrupolar interaction effect¹⁹. Upon decreasing the temperature from 260 K, both K_a and K_c

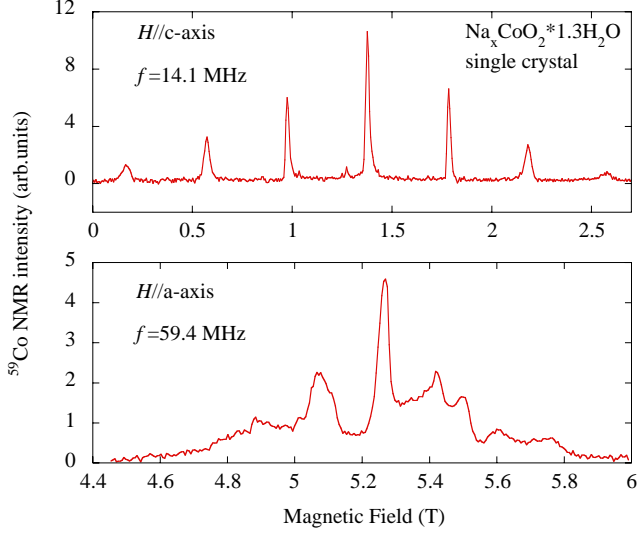


FIG. 1: (Color online) ^{59}Co NMR spectra in $\text{Na}_{0.42}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ at $T=4.2$ K with $H \parallel c$ -axis at 14.1 MHz (upper panel) and with $H \parallel a$ -axis at 59.4 MHz (lower panel).

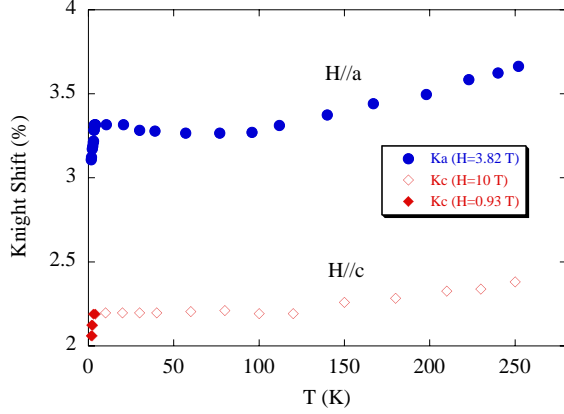


FIG. 2: (Color online) Temperature dependence of the Knight shift K_a with the field applied along the a -axis, and K_c with the field applied along the c -axis.

decrease, but tend to be saturated below $T=100$ K before superconductivity sets in. The decrease of the Knight shift with decreasing temperature is consistent with the bulk susceptibility results reported by Foo *et al*²⁰ and also for the sample used in the present study²¹, although a previous measurement has failed to detect the temperature dependence²². Below, we show that the spin shift is quite large and can be used to distinguish the pairing symmetry in the superconducting state.

The Knight shift is composed of the spin part K^s due to the spin susceptibility (χ^s) and the orbital part

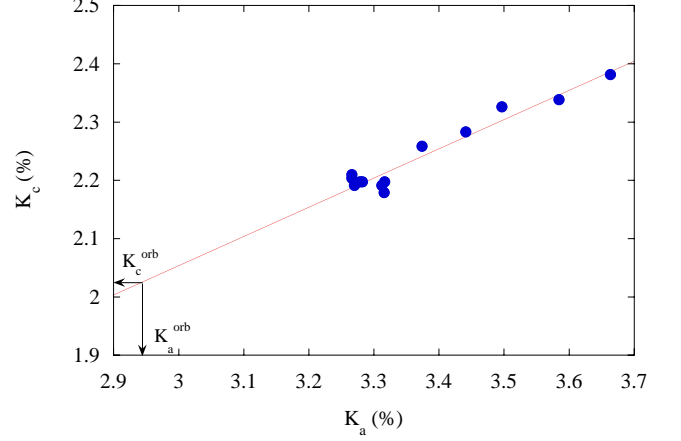


FIG. 3: (Color online) The plot of K_c vs K_a . The straight line is the best fit to the data which gives $K_a^s = 2K_c^s$. The arrows indicate the estimated orbital contributions to the shifts (see text).

K^{orb} due to the orbital susceptibility (χ^{orb}) which is T -independent.

$$K = K^{orb} + K^s \quad (1)$$

$$K^s = A^{hf} \chi^s \quad (2)$$

where A^{hf} is the hyperfine coupling constant between the nuclear and the electron spins. Figure 3 shows the plot of K_c versus K_a . The straight line is a fitting to the data which gives $K_c = 0.5K_a + \text{const.}$, which means that $K_a^s = 2K_c^s$. The temperature dependence of the Knight shift is similar to the case of electron-doped cuprate superconductor $(\text{Pr}_{0.91}\text{La}_{0.09})_2\text{CeCuO}_4$, in which K_a also decreases with decreasing temperature and becomes a constant below $T=60$ K²³.

Let us focus on the temperature dependence of the Knight shift below T_c . First, both K_a and K_c decrease below $T_c(H)$, as can be seen in Figure 4 that shows the enlarged part of the shift below $T=5$ K for $H(3.82 \text{ T}) \parallel a$ -axis and $H(0.93 \text{ T}) \parallel c$ -axis. $T_c(H \parallel a)$ and $T_c(H \parallel c)$ at which the shift decreases is 3.5 K and 3.1 K, respectively, which is in good agreement with the report by Chou *et al*²⁴. Figure 5 compares two of the spectra above and below T_c , respectively, for both field configurations. The reduction of K_a and K_c at $T=1.6$ K amounts to 0.2% and 0.13%, respectively. The smaller reduction of K_c is mostly due to the smaller spin part K_c^s . For $H \parallel c$ -axis, we have also carried out measurements at 14.1 MHz ($H \sim 1.38 \text{ T}$), and found detectable shift change between $T_c(H)$ and $T=1.6$ K. Namely, $\Delta K_c = K(2.8 \text{ K}) - K(1.6 \text{ K}) = 0.05\%$. We have further measured the shift at 7.1 MHz ($H \sim 0.69 \text{ T}$) in another sample with $T_c=3.6$ K, and found $\Delta K_c = K(3.0 \text{ K}) - K(1.6 \text{ K}) = 0.15\%$. In all cases, we have confirmed that the ^{23}Na NMR spectrum has a

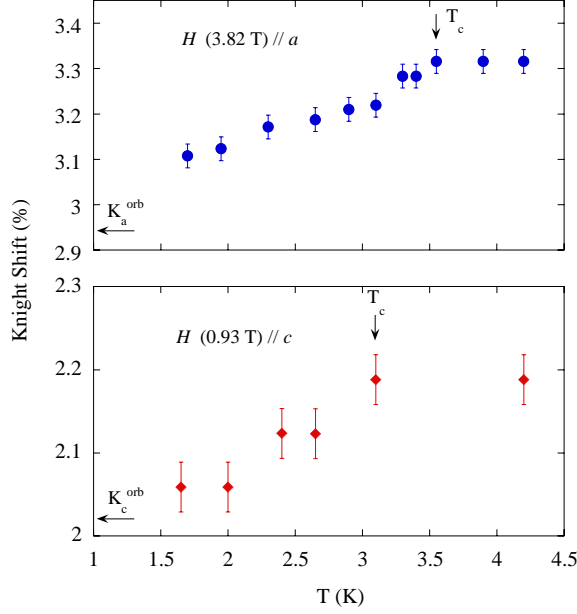


FIG. 4: (Color online) The enlarged part of the ^{59}Co Knight shift at low temperatures. The vertical arrows indicate $T_c(H)$ at the respective external fields. The horizontal arrows indicated $K_{a,c}^{\text{orb}}$, the shift due to orbital susceptibility (see text for the estimation).

full width at half maximum (FWHM) of 20 kHz, and does not move appreciably across T_c within the experimental accuracy. Assuming that one can detect a change of one tenth the FWHM in the ^{23}Na spectrum, we estimate that the contribution to the Knight shift due to the diamagnetism effect (K^{dia}) in the vortex state is no larger than 0.02%²⁵. Therefore the reduction of K_a and K_c below $T_c(H)$ is due predominantly to the reduction of the spin susceptibility. This result indicates that the spin pairing in the superconducting state is in the *singlet* state.

Among the existing theoretical models, the *p*-wave⁴, *f*-wave^{5,6,7,8} states and the odd-frequency *s*-wave state¹⁰ are spin triplet states, while the chiral *d*-wave state^{2,3} is a spin singlet but fully gapped state. They are not in agreement with our finding, but probably the *i*-wave state⁹ is an exception. However, a pure *d*-wave state with line nodes in the gap function appears to be consistent with both the Knight shift data and the T^3 dependence of $1/T_1$ ¹². Generally speaking, a state with lower angular momentum (*i.e.* *d*-wave) is energetically more favorable compared to its higher angular momentum counterparts (*i.e.* *i*-wave). In addition, there are two conditions pertinent to the present case that favor a pure *d*-wave state. Firstly, although a fully-gapped $d_1 + id_2$ state is predicted for an exact triangular lattice^{2,3}, anisotropy (10~20%) of the lattice will stabilize a pure *d*-wave state²⁶. Secondly, it has been found that the spin order in $\text{Na}_{0.5}\text{CoO}_2$ is antiferromagnetic, with alternative rows

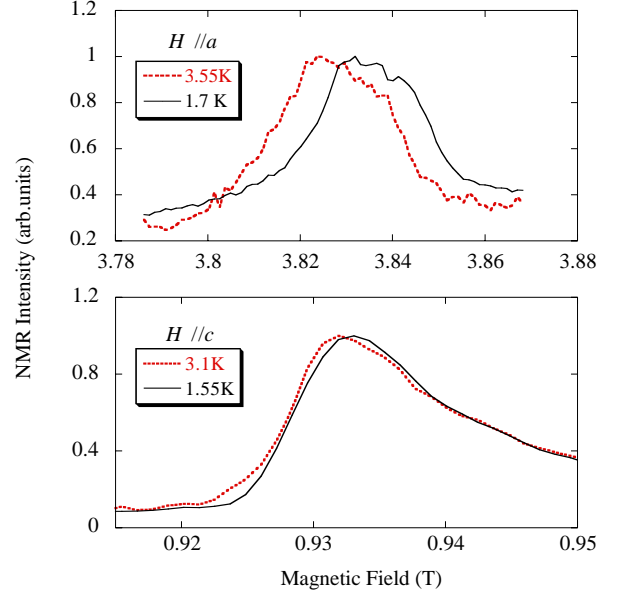


FIG. 5: (Color online) Comparison of the spectra above T_c (broken curves) and below T_c (solid curves) at different field configurations.

of Co^{4+} ($s=1/2$) and Co^{3+} ($s=0$) in the CoO_2 plane²⁷. In other words, the triangles with regards to the spin configuration are effectively squared. In fact, both the Knight shift found in this study and the temperature dependence of $1/T_1T$ in the normal state in $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ ($x = 0.25 \sim 0.35$)¹² point to the presence of antiferromagnetic correlations, which would favor *d*-wave pairing.

Next we attempt to separate the K^s and K^{orb} from the observed shift data, and argue that the data below T_c can be consistently accounted for by an anisotropic superconducting state with nodes in the gap function and with spin singlet pairing. In *s*-wave superconductors with isotropic gap, the spin susceptibility outside the vortex cores vanishes completely at a temperature far below T_c . In anisotropic superconductors with nodes in the gap function, however, the spin susceptibility outside the vortex cores can remain a finite value since the quasiparticles state can be extended from the vortex core along the nodal directions²⁸. Volovik pointed out that the density of such delocalized quasiparticle state, N_V , is proportional to $\sqrt{H/H_{c2}}$ where H_{c2} is the upper critical field²⁸. Indeed, in an overdoped cuprate superconductor, it has been found that $N_V/N_0 \sim 0.7\sqrt{H/H_{c2}}$ (ref.²⁹), where N_0 is the density of states (DOS) in the normal state. Note that the coefficient 0.7 is less than 1, because NMR only probes the DOS outside the vortex cores. If we use the data of $H_{c2}^a(0)=8$ T and $H_{c2}^c(0)=4$ T by Chou *et al*²⁴ and the same N_V as in the cuprate, we obtain $K_a^{\text{orb}}=2.94\%$ from the relation $0.7\sqrt{H/H_{c2}}(K_a(4.2\text{ K})-K_a^{\text{orb}})=K_a(1.6\text{ K})-K_a^{\text{orb}}$. Once K_a^{orb} is known, one obtains readily $K_c^{\text{orb}}=2.02\%$ from the K_c vs K_a plot in

Fig. 3. Such estimate consistently explains the K_c result; the H -induced shift at the lowest temperature due to $N_V(H \parallel c)$ is calculated to be 0.05%, which is in fair agreement with the experimental result of $0.04 \pm 0.03\%$. Note that $K_a^s \geq 0.72\%$, which is about two times the spin shift in cuprate superconductors^{23,30}. Finally, we comment that the estimated $K_{a,c}^{orb}$ agrees fairly well with that independently estimated from the Knight shift vs DC susceptibility ($Kvs\chi$) plot³¹.

In conclusion, the ^{59}Co NMR measurements in a single crystal of $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ ($T_c = 4.25$ K) allowed us, for the first time, to obtain a complete data set of the Knight

shift. We found that the shift due to the spin susceptibility is substantially large (0.72% along the a -axis) and anisotropic, with $K_a^s = 2K_c^s$. Both K_a^s and K_c^s decrease below T_c , indicating that the spin pairing of the Cooper pairs is in the singlet state. Our work that settled the electron pairing symmetry in the superconducting state should help pave the first step toward understanding the mechanism of the superconductivity in this new class of materials.

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